ENVIRONMENTAL ANALYSIS

Determination of Bisphenol A in Sewage Effluent and Sludge by Solid-Phase and Supercritical Fluid Extraction and Gas Chromatography/Mass Spectrometry

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Methods have been developed for the determination of bisphenol A (BPA) residues in municipal sewage and sludge samples. BPA in wastewater samples was enriched with a C_{18} solid-phase extraction cartridge, eluted with acetone, and converted to the pentafluoropropionyl derivative. For sludge samples, BPA was acetylated and extracted with supercritical carbon dioxide. In both cases, BPA-d_{16} was used as a surrogate to monitor extraction efficiency. Final analyses of derivatized sample extracts were performed by gas chromatography/mass spectrometry operating in the electron impact mode. For water samples, mean recoveries and standard deviations were 89 ± 6, 94 ± 4, and 85 ± 7% at fortification levels of 1, 0.1, and 0.025 μg/L, respectively, with a method detection limit of 0.006 μg/L. For solid waste samples, mean recoveries and standard deviations were 93 ± 5 and 92 ± 6% at fortification levels of 2.5 and 0.25 μg/g, respectively, and the method detection limit was 0.05 μg/g. For the Canadian samples under investigation, concentrations of BPA ranged from 49.9 to 0.031 μg/L in sewage influent and effluent, and from 36.7 to 0.104 μg/g in sludge.

Bisphenol A (BPA or 4,4′-isopropylidenediphenol) is manufactured in large quantities in the United States from the acid-catalyzed condensation of phenol with acetone. In recent years, the demand for BPA has increased steadily, from 0.73 billion kg in 1995 to 0.82 billion kg in 1998. By 2002, the projected demand will exceed 1 billion kg, representing 5% annual growth (1). BPA is the building block of many resins. About 63% of BPA produced today is used worldwide for the manufacture of polycarbonate plastic resins; 27% for epoxy resins; and the remaining 10% for miscellaneous products such as flame retardants (mainly tetrabromobisphenol A) and unsaturated polyester, polysulfone, polyetherimide, and polyarylate resins (1).

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Aquatic toxicity studies of BPA indicated an acute toxicity (effect/lethal concentration) varying from 1 mg/L for algae (*Skeletonoma costatum*) to 15.5 mg/L for invertebrates (*Daphnia magna*; 2). Several biodegradation studies demonstrated rapid breakdown of BPA under acclimated conditions. In one study, > 90% degradation was observed within 4 days in a BPA chemical plant discharge and 2 other surface water samples (2). Another study showed that BPA biodegraded rapidly (in a few hours) through the action of a gram-negative, aerobic bacterium (strain MV1), and nearly 60% of the carbon in BPA was mineralized to CO_2 (3). This novel bacterium used BPA as a sole source of carbon and energy and was isolated from a sludge enrichment taken from a wastewater treatment plant at a plastic manufacturing facility. In contrast, studies performed under unacclimated conditions indicated < 1% degradation in 28 days (4, 5).

Recently, a great deal of attention has been focused on the estrogenic activities of BPA, which were first identified by Dodds and Lawson (6). These findings were later confirmed by the work of Bitman and Cecil (7), Bond et al. (8), and Krishnan et al. (9). In the last case, BPA was found to induce progesterone receptors in cultured human breast cancer cells (MCF-7) at a rate 5000 times less potent than 17β-estradiol (E_2). BPA also binds to estrogen receptors with affinities 2000 times lower than that of E_2 and thus, is one of the more potent anthropogenic estrogen mimics (10). As a result, some concerns have arisen about the possibility of BPA leaching from food packaging materials and beverage containers in which polycarbonate plastic resins and epoxy resins have been used in food contact applications (11).

BPA may find its way into the environment through the thermal degradation of many plastic products, or from the discharge of BPA manufacturing or processing plants. Few analytical methods are available for the determination of BPA in environmental samples. A liquid chromatographic method with electrochemical detection was developed for the determination of BPA in air (12). More recently, a gas chromatographic/mass spectrometric method was reported for the detection of BPA in water samples (13); however, because of the relatively high method detection limit (MDL) of 0.6 μg/L, no BPA was found in any of the seawater and spring water samples tested (13). No procedure has been published for the ex-

traction of BPA in solid waste samples. For these reasons, very few data on the occurrence and fate of BPA in sewage and sludge samples are presently available.

In order to establish a database on the occurrence of BPA and evaluate its environmental fate in Canada, new and more sensitive analytical methods are required. The present paper describes methods based on established solid-phase extraction (SPE) and supercritical fluid extraction (SFE) techniques in combination with gas chromatography/mass spectrometry (GC/MS) for the determination of BPA in municipal sewage and sludge samples. This work is another example of our continuing research on the identification, occurrence, and fate of endocrine-disrupting chemicals in sewage samples (14–17).

Experimental

Chemicals and Reagents

BPA (99+%), BPA-d_{16} (98 atom % D), pentafluoropropionic anhydride (PFPA, 99%), acetic anhydride, and formaldehyde (37% solution in water) were obtained from Aldrich Chemical Co. (Milwaukee, WI). For the highest derivatization yields, acetic anhydride was triple-distilled before use. All other chemicals were used without further purification. Stock solutions of BPA (1000 μg/mL) and BPA-d_{16} (500 μg/mL) were prepared in acetone. Working solutions of these phenols at lower concentrations were also prepared in acetone by serial dilution. Celite and anhydrous potassium carbonate were from Fisher Scientific Co. (Toronto, ON, Canada).

Distilled-in-glass grade solvents including acetone, dichloromethane (DCM), ethyl acetate, isooctane, methyl *tert*-butyl ether (MTBE), and petroleum ether (bp = 30°–60°C) were purchased from Caledon Laboratories Ltd. (Georgetown, ON, Canada) or Burdick & Jackson Laboratories (Muskegon, MI). Supercritical carbon dioxide (SFE grade) without helium head pressure was manufactured by Air Products (Bramptom, ON, Canada).

Sample Collection and Preservation

Composite (24 h) samples of raw sewage and final effluent in 1 L aliquots were collected in late 1998 and early 1999. For sewage treatment plants located in southern Ontario, samples were kept at 4°C in the dark without preservative because they were extracted within 24 h after collection. For samples collected from plants elsewhere, 10 mL 37% formaldehyde solution was added to each sample at the time of collection. They were kept cold in transit (by overnight courier) and kept at 4°C in the dark at the laboratory. Grab samples of raw and digested sewage sludge were unpreserved. They were air-dried, pulverized, passed through a 100 mesh sieve, and kept at room temperature.

(*Caution*: Because of the presence of bacteria, viruses, and parasites that may pose a health hazard to workers, protective equipment must be used for the collection and handling of sewage samples. Workers should also have proper immunization as recommended by the local health authorities.)

Extraction, Cleanup, and Derivatization

(**a**) *SPE of effluent samples*.—Each sewage sample was filtered through a 47 mm Whatman GF/C filter with a pore size of 1.2 μm, connected to an all-glass funnel support assembly. In this process, a filter aid such as Celite 545 was used to minimize plugging of the filter. An aliquot of the sample (typically 250 mL) was measured, 500 ng BPA-d_{16} was added as a surrogate, and the mixture was acidified with 1N HCl to pH 3.

Before extraction, each C_{18} SPE cartridge (ENVI-18, Supelco 505706, Bellefonte, PA) was conditioned with 5 mL acetone, 5 mL methanol, and 10 mL pH 3 water on an SPE manifold (Supelco Visiprep DL 5-7044) according to the manufacturer's instructions. The sample filtrate was then applied to the cartridge via a siphon tube and an adaptor (Supelco 5-7275). An average flow rate of 10 mL/min was maintained by adjusting the vacuum to ca 50 kPa. When the extraction was completed, the cartridge was dried under vacuum for 5 min. A 5 mL portion of acetone–water (1 + 4, v/v), in 2 equal fractions, was used to rinse the cartridge, and the washes were discarded. BPA was removed from the cartridge by eluting with 10 mL acetone.

The acetone extract was gently evaporated by a stream of nitrogen on a 40°C water bath to 200–300 μL, at which point the residue was mainly water. BPA was then back-extracted into three 2 mL portions of ethyl acetate. The combined ethyl acetate layer was filtered through a 3 cm Celite column prepared in a disposable Pasteur pipet. (*Caution*: The use of anhydrous sodium sulfate at this point could lead to a lower recovery because of adsorption.) The extract was evaporated to 200 μL before it was applied to a cleanup column packed with 5 cm 5% deactivated silica gel in a disposable Pasteur pipet that had been prewetted with 3 mL petroleum ether. The column was then eluted with 10 mL acetone–hexane (1 + 2, v/v) for the removal of BPA. (*Note*: The silica gel cleanup step can be omitted for less contaminated samples such as those from some surface waters.)

The acetone–hexane extract was evaporated to dryness. The phenol was derivatized with 50 μL PFPA in the presence of 50 μL ethyl acetate at room temperature. After 20 min, 3 mL petroleum ether and 3 mL 1% K_2CO_3 solution were added to remove excessive reagent and acids. The mixture was mixed on a Vortex mixer, the upper layer was removed, and the aqueous layer was extracted twice with 3 mL portions of petroleum ether. The combined organic layer was passed through a column of anhydrous sodium sulfate in a Pasteur pipet, evaporated, and exchanged into 1 mL isooctane for GC/MS analysis. Calibration standards of the pentafluoropropionyl (PFP) derivative of BPA were prepared by reacting known amounts of the authentic standard with PFPA, as described above.

(**b**) *Supercritical carbon dioxide extraction of sludge*.—BPA in sludge was extracted and acetylated by an SFE procedure similar to that developed for the determination of nonylphenol in sewage sludge (14) by the use of a 7680T extractor (Hewlett-Packard, Little Falls, DE). Before extraction, 50 μL of a BPA-d_{16} solution at 10 μg/mL was

added to a 100–250 mg sample as a surrogate standard. A 200 μL portion of acetic anhydride and 30 μL triethylamine were also added to the sludge to facilitate the in situ acetylation. The sample was extracted at 80°C with nonmodified supercritical CO_2 with a density of 0.79 g/mL (pressure, 37 MPa). The static and dynamic extraction times were 15 and 10 min, respectively, and the flow rate of supercritical CO_2 was 2 mL/min during the dynamic extraction. At the end of the extraction, the BPA diacetate adsorbed on the octadecylsilane-bonded silica (ODS) trap was eluted with 1.7 and 1.0 mL acetone in 2 rinses.

The combined sludge extract in acetone was evaporated to dryness, and then 3 mL petroleum ether and 3 mL 1% K_2CO_3 solution were added. The mixture was shaken in a Vortex mixer for 1 min, and the upper organic layer was removed. A centrifuge was used when an emulsion formed. Extraction of the aqueous layer was repeated twice, with 3 mL portions of petroleum ether. The combined organic layer was passed through an anhydrous sodium sulfate column and evaporated to ca 1 mL.

The concentrated extract containing BPA diacetate was cleaned up on a 5 cm 5% deactivated silica gel column prepared in a disposable Pasteur pipet. After the column was moistened with 3 mL petroleum ether, the extract was applied to the column, and the derivatized phenol was eluted with 10 mL DCM. The latter was evaporated and exchanged into 1 mL isooctane for GC/MS analysis.

Calibration standards for the acetate derivative of BPA were prepared by acetylating known amounts of the authentic standard (no solvent) with 200 μL acetic anhydride and 10 μL pyridine at 60°C for 30 min. Although a silica gel column cleanup was not needed, the reaction products were washed with 1% K_2CO_3 solution, as described above for the PFP derivatives.

(**c**) *Accelerated solvent extraction (ASE) of sludge*.—ASE of BPA from sludge samples was carried out with a Dionex ASE 200 extractor. Typically, 0.25 g sample and the surrogate standard, placed in a 22 mL stainless steel extraction cell, were extracted with DCM–acetone (1 + 1, v/v) in 3 cycles. The oven temperature was 100°C, and the pressure was 12.7 MPa or 1800 psi. The oven heat-up time was 5 min, and the static time was 10 min. Flush volume was 75% of the extraction cell volume.

An aliquot of the extract was evaporated to dryness and redissolved in 200 μL ethyl acetate. The extract was then cleaned up on a 5% deactivated silica gel column and derivatized with PFPA as described above for effluent samples.

GC/MS Determination

GC/MS analyses of BPA derivatives were performed with a Hewlett-Packard 6890 gas chromatograph equipped with a 5973 mass selective detector operating in the electron impact (EI) mode. A 30 m × 0.25 mm id HP-5-MS column with 0.25 μm film thickness was used for chromatographic separation. GC conditions for the PFP derivatives were initial oven temperature, 70°C; initial time, 1.0 min; programming rates, from 70° to 210°C at 30°C/min, and then to 240°C at 2°C/min. A post-analysis baking at 270°C for 4 min was also applied to the column. The carrier gas (helium) flow rate was held constant at 1.1 mL/min with a linear velocity of 39 cm/s. For the acetate derivatives, the GC conditions were initial oven temperature, 70°C with a 1 min hold; programming rates, from 70° to 200°C at 30°C/min, and then to 260°C at 5°C/min with a 4 min hold at the final temperature. The constant carrier gas (helium) flow rate was set at 0.9 mL/min with a linear velocity of 35 cm/s. In both cases, 1 μL splitless injections were made by a Hewlett-Packard 7683 autosampler with a splitless time of 1 min.

The detector was tuned with perfluorotributylamine (PFTBA) by using the autotune program. The electron energy was 70 eV, and the electron multiplier was operating at 200 V above the autotune value with the high energy dynode on. Temperatures for the MS source and quadrupole were 230° and 150°C, respectively. Full-scan mass spectra were recorded from *m/z* 50 to 550. The following ions were used for quantitative selected ion monitoring (SIM) of the PFP derivatives: *m/z* 520 and 505 (BPA) and *m/z* 534 and 516 (BPA-d_{16}). In the case of the acetate derivatives, the ions at *m/z* 312 and 228 (BPA) and *m/z* 326 and 242 (BPA-d_{16}) were used.

Fortified samples were quantitated, by the external standard method, by comparison with a derivatized standard containing the same amount of BPA as in the spiked samples. Sewage effluent and sludge samples were also quantitated by external standard method using a 2-point standard curve (50 and 250 pg/μL). Sample extracts with BPA concentrations > 250 pg/μL were diluted and rerun.

Results and Discussion

PFP and Acetyl Derivatives of BPA and Their MS Properties

In this work, both PFP and acetyl derivatives were used for the determination of BPA. In addition to better chromatography, another advantage of derivatizing BPA before GC/MS analysis is greater detector selectivity. The latter was achieved by shifting the more volatile derivatives to shorter retention times and concurrently monitoring characteristic ions at higher masses. This combination generally leads to reduced interference in the final analysis. This approach is particularly beneficial for the PFP derivatives of BPA and its labeled analog, for which intense characteristic ions above *m/z* 500 were monitored (about 300 daltons higher than the *m/z* values for the parent compound) at relatively low elution temperatures.

The PFP derivative was used for the effluent samples because it offered better sensitivity than did the acetyl derivative. The latter was selected for sludge samples so that the method would be compatible with a previously developed, in situ acetylation SFE procedure for the determination of nonylphenol in the same type of matrix. If another extraction technique (e.g., Soxhlet, etc.) is selected for use with sludge samples, an off-line derivatization procedure with PFPA may be used instead.

PFPA reacted readily with the unlabeled and labeled BPA at room temperature, and in both cases a single product was

formed. The relative standard deviation (RSD, as determined by the peak area in full-scan GC/MS runs) for a triplicate derivatization of BPA at the 10 μg level was 5.4%. Solutions of the BPA derivatives in isooctane were stable for ≥ 4 weeks at –20°C in the dark.

The EI mass spectrum for the PFP derivative of BPA (Figure 1A) displayed a molecular ion (M^+) at *m/z* 520, indicating that both phenolic groups were acylated. Other characteristic ions observed included *m/z* 505 or $(M\text{-}CH_3)^+$ (base peak), *m/z* 281 $(M\text{-}239)^+$ or $(M\text{-}C_6H_4OCOC_2F_5)^+$, as well as *m/z* 265, a fragment arising from a neutral loss of CH_4 from the *m/z* 281 species. Similarly, the PFP derivative of labeled BPA-d_{16} (Figure 1B) displayed characteristic ions at *m/z* 534 (M^+), *m/z* 516 $(M\text{-}CD_3)^+$ (base peak), *m/z* 291 $(M\text{-}C_6D_4OCOC_2F_5)^+$ or $(M\text{-}243)^+$, and *m/z* 271 $(M\text{-}243\text{-}CD_4)^+$.

Acetylation of BPA and BPA-d_{16} also produced, in each case, a single product with a diacetate structure, as indicated by a molecular ion (M^+) occurring at *m/z* 312 and 326, respectively. Similar to the PFP analogs, these products were also stable for weeks at –20°C in the dark, and the reaction was likewise reproducible (RSD of 3.5% for triplicate derivatization). Other characteristic ions of BPA diacetate (Figure 2A) included $(M\text{-}CH_2CO)^+$ at *m/z* 270, $(M\text{-}CH_2CO\text{-}CH_2CO)^+$ at *m/z* 228, and $(M\text{-}CH_2CO\text{-}CH_2CO\text{-}CH_3)^+$ (base peak) at *m/z* 213. Similarly, characteristic ions at *m/z* 284, 242, and 224 (base peak) derived from the same fragmentation pattern were observed for the

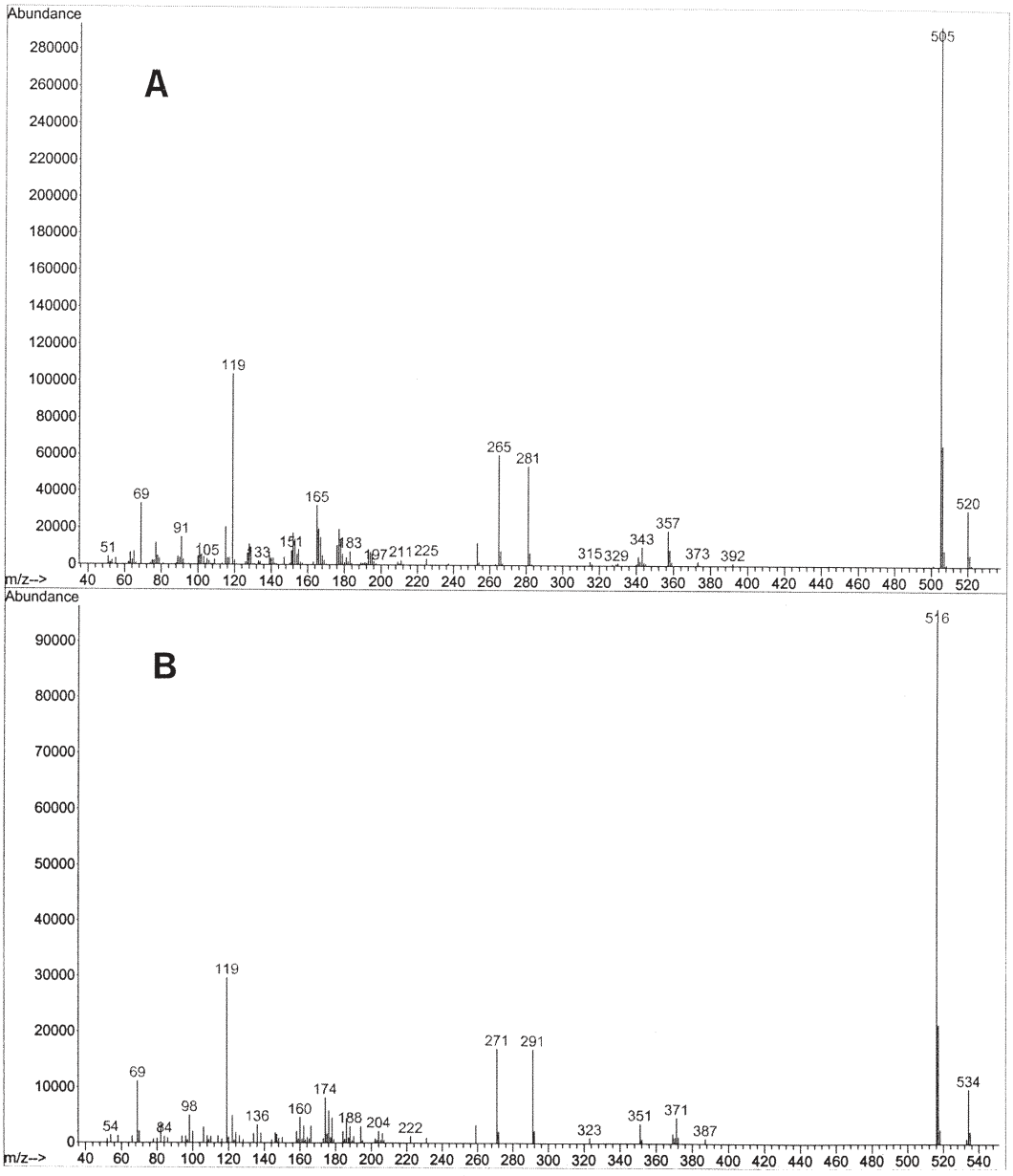

Figure 1. Full-scan mass spectra of the PFP derivatives of (A) BPA and (B) BPA-d_{16}.

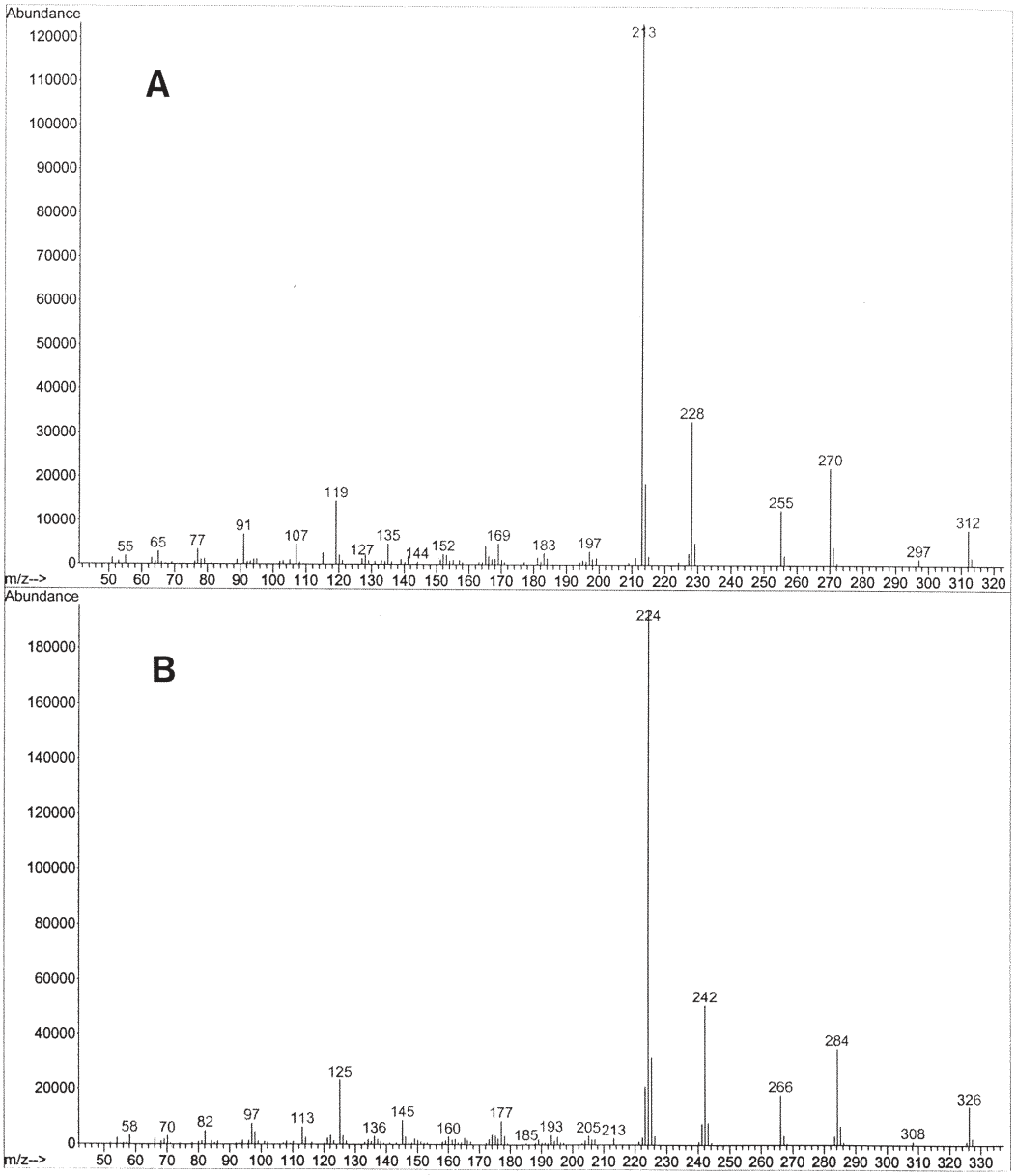

Figure 2. Full-scan mass spectra of the acetyl derivatives of (A) BPA and (B) BPA-d_{16}.

Table 1. Recovery of BPA and BPA-d_{16} from fortified samples

Sample	No. of replicates	BPA spiking level, μg/L	Mean BPA recovered, μg/L (%)	SD, μg/L[a]	BPA-d_{16} level, μg/L	Mean BPA-d_{16} recovered, μg/L (%)	SD, μg/L
Distilled water	4	1.0	0.89 (89)	0.063	2	1.81 (90)	0.055
Distilled water	4	0.10	0.094 (94)	0.0044	2	1.90 (95)	0.96
Distilled water	7	0.025	0.021 (84)	0.0018	2	1.74 (87)	0.088
Sediment	7	2.5[b]	2.33[b] (93)	0.125[b]	5[b]	4.80[b] (96)	0.24[b]
Sediment	7	0.25[b]	0.23[b] (92)	0.016[b]	5[b]	4.73[b] (94)	0.28[b]

[a] SD = standard deviation.

[b] μg/g.

Table 2. Mean levels of BPA found and recoveries of BPA-d_{16} from field samples by various extraction procedures[a]

Sample[b]	Mean BPA found, ± SD	Mean recovery of BPA-d_{16} ± SD, %
A (influent by SPE)	4.99 ± 0.04 μg/L	105 ± 2[c]
B (effluent by SPE)	0.277 ± 0.003 μg/L	103 ± 2[c]
C (sludge by SFE)	1.51 ± 0.09 μg/g[d]	88 ± 7[e]
C (sludge by ASE)	1.36 ± 0.02 μg/g[d]	98 ± 2[e]
D (sludge by SFE)	36.7 ± 1.6 μg/g[d]	93 ± 5[e]
D (sludge by ASE)	35.8 ± 1.8 μg/g[d]	97 ± 3[e]

[a] $n = 3$.

[b] Samples A and B were collected from Vancouver, BC; sample C, from Toronto, ON; and sample D, from Guelph, ON. The samples were selected to validate the procedures because they covered the wide range of BPA levels found in field samples.

[c] Surrogate spiking level of 2 μg/L.

[d] On a dry weight basis.

[e] Surrogate spiking level of 5 μg/g.

acetyl derivative of the labeled compound (Figure 2B). It should be noted that although the $(M\text{-}CH_3)^+/(M\text{-}CD_3)^+$ ion was the base peak in the EI spectrum for the PFP derivative of BPA/BPA-d_{16}, the same fragment was barely observable for the acetyl analogs.

Detector Linearity and Quantitation Limit

Linearity of the response of the mass selective detector to the PFP derivative of BPA was assessed by injecting standard solutions in isooctane at the following concentrations: 1000, 250, 100, 25, and 2.5 pg/μL. In the SIM mode with 2 ions monitored (*m/z* 505 and 520), the detector response was linear (r^2 = 0.998) over the range 2.5–250 pg injected. The quantitation limit was < 0.4 pg injected (signal-to-noise ratio [S/N], 10:1). For the acetate derivative for which the *m/z* 312 and 228 ions were monitored, the detector response was linear ($r^2 = 0.999$) over the range 10–500 pg injected. The quantitation limit was 2.7 pg injected (S/N, 10:1). The detector sensitivity for BPA diacetate could have been improved if the ion *m/z* 213 (base peak, Figure 2A) had been used in the SIM runs. However, it was not used because of observed interference from this ion in the analysis of sludge extracts.

Validation of Preconcentration Procedures

(**a**) *SPE of water samples*.—BPA at 3 spiking levels was recovered from replicates of distilled water by using the SPE procedure (Table 1). At concentrations of 1, 0.1, and 0.025 μg/L, the mean recovery of BPA was between 84 and 94%. The mean recovery of BPA-d_{16} at the constant spiking level of 2 μg/L was 91%. Based on the results obtained at the lowest spiking level (0.025 μg/L), the calculated MDL (18) at 0.006 μg/L (MDL = S × *t*, where S = standard deviation = 0.0018 μg/L, and *t* = Student's *t*-value = 3.14 for 7 replicates) was 100 times better than that (0.6 μg/L) reported earlier (12). Recovery experiments were not performed on sewage effluents, because of the lack of a field sample with a low BPA blank. However, replicate extraction of some wastewater samples generated results with good precision (Table 2). Consistent recoveries (ranging from 87 to 107%) of the surrogate, BPA-d_{16}, from all effluent samples ($n = 47$) also implied good accuracy of the procedure.

The performance of the present SPE procedure was further evaluated against a solvent (MTBE) extraction procedure. In this case, the concentration of dissolved BPA in a saturated solution prepared at room temperature (22°–24°C) was determined by replicate extraction using the above procedures. The solubility of BPA found was 253 ± 14 mg/L ($n = 4$) as determined by the SPE technique and 257 ± 9 mg/L ($n = 3$) as determined by the solvent extraction technique. Because the numbers are basically the same within experimental errors, it was concluded that SPE is as effective as solvent extraction for the preconcentration of dissolved BPA in aqueous sam-

Table 3. BPA levels in samples[a] from municipal sewage treatment plants

Plant[b]	Sampling date	Influent, μg/L	Final effluent, μg/L	Raw sludge, μg/g[c]	Digested sludge, μg/g[c]
Burlington	1/11/99	0.193	0.031	NA[d]	0.316
Calgary A	3/02/99	0.278	0.147	NA	0.789
Calgary B	3/02/99	0.219	0.035	NA	0.795
Galt	5/13/99	0.954	0.201	NA	1.59
Toronto A	5/13/99	0.232	0.048	0.197	0.268
Toronto B	5/31/99	2.44	0.112	8.73	12.5
Toronto C	5/31/99	0.405	0.183	NA	1.13
Toronto D	6/01/99	0.889	0.223	1.72	NA

[a] All influents and effluents are 24 h composite samples. All sludges are grab samples.

[b] There are 4 sewage treatment plants in Toronto and 2 in Calgary.

[c] On a dry weight basis.

[d] NA = sample not available.

ples. The solubility of BPA determined in this work is also consistent with the literature value of 120–300 mg/L (1, 2).

(**b**) *SFE of solid samples*.—Although the technique has not been widely used, the in situ acetylation of phenols under supercritical CO_2 extraction conditions is a very efficient method for the determination of chlorinated phenols in sediment and soil (19, 20) and alkylphenols in sewage sludge (14). In these cases, phenolic compounds are extracted by supercritical CO_2 and, at the same time, acetylated in the presence of small amounts of acetic anhydride and triethylamine. At the beginning of this work, we attempted the extraction of BPA from sewage sludge by applying the procedure developed previously for the determination of 4-nonylphenol and 4-*tert*-octylphenol in the same matrix. Although the results were encouraging because BPA was converted to its diacetylated derivative, the recoveries of BPA and the deuterated surrogate from spiked samples were only 45–80%. Longer extraction times and different extraction temperatures (60° or 100°C) did not improve recoveries. Although the unextracted BPA could have been recovered by a second extraction with fresh reagents, it was accomplished more conveniently by using excess acetic anhydride (200 μL) at the start of the extraction. When a previously solvent-extracted sediment sample was spiked, the mean recoveries of BPA were

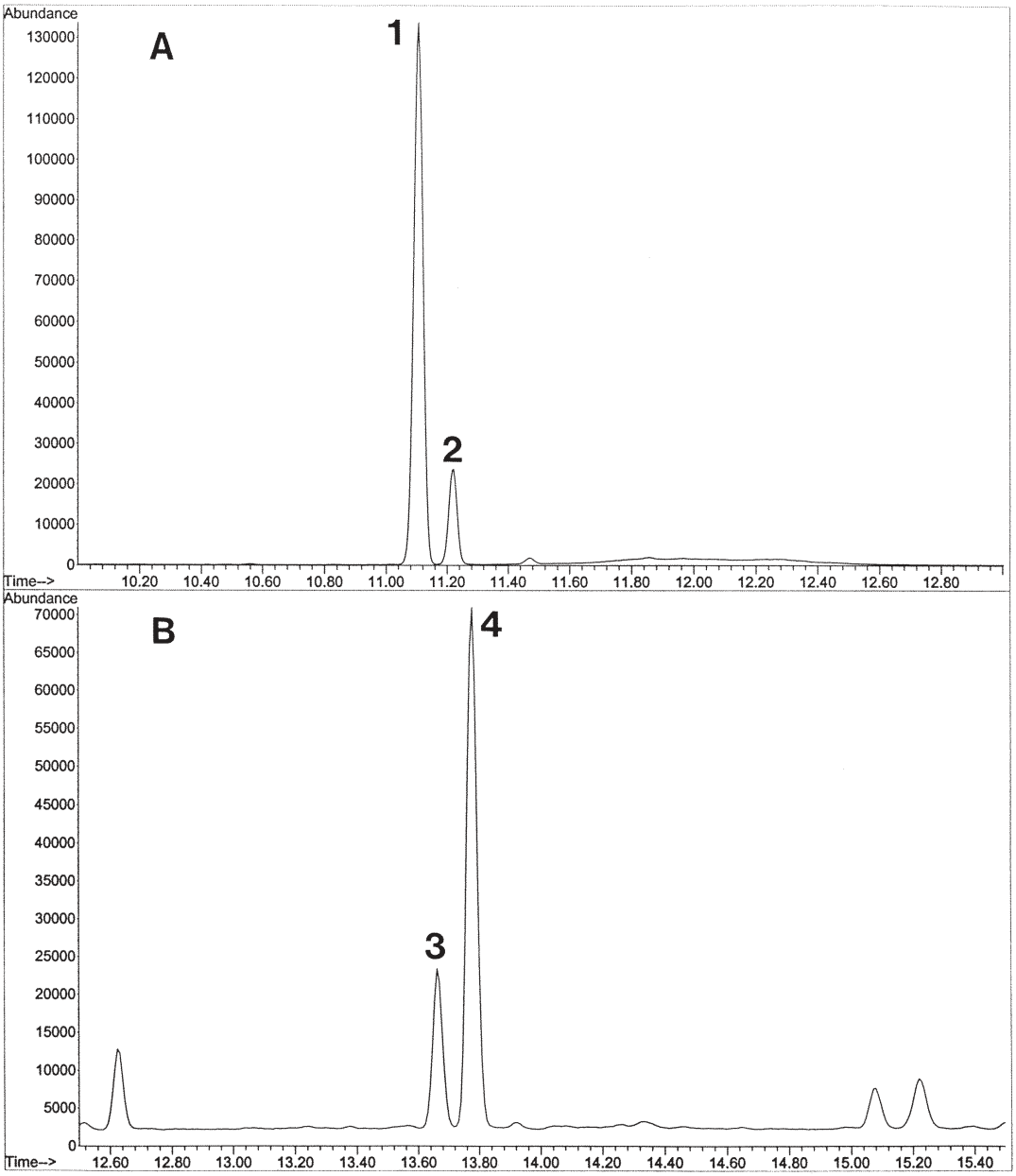

Figure 3. Total ion current chromatograms of the extracts of (A) an influent from Burlington and (B) a sludge from Toronto, with BPA levels at 0.193 μg/L and 12.5 μg/g, respectively. Peaks: 1 = BPA-d_{16}-PFP, 2 = BPA-PFP, 3 = BPA-d_{16}-diacetate, and 4 = BPA-diacetate.

> 90% at fortification levels of 2.5 and 0.25 μg/g (Table 1). The calculated MDL was 0.05 μg/g (0.016 μg/g × 3.14).

The efficiency of the SFE procedure was also compared with that of a solvent extraction procedure using an accelerated solvent extractor. In the latter case, a generic procedure designed for the extraction of priority pollutants (basic, neutral, and acidic) was used (21). On the basis of the results of replicate extractions of 2 sewage sludge samples (Table 2), it was concluded that SFE and ASE produced comparable results for the determination of BPA in sludge samples.

Cleanup and Procedure Blank

Because of the high level of contamination in sewage samples, cleanup steps were necessary to reduce interference in the final determination of the target contaminant. For influent and effluent samples, the more polar coextractives such as dyes and pigments were removed by elution of the ODS cartridge with acetone–water (1 + 4 v/v) before elution of BPA with acetone. The BPA extract was further cleaned up on a 5% deactivated silica gel column before chemical derivatization. The same column was also used for cleanup of the SFE extracts of sludge samples. Procedure blanks were determined with organic-free water (SPE) and high-purity Celite (SFE). No BPA was detected in those cases.

Applications to Environmental Samples

These newly developed methods have been applied to the determination of BPA in municipal wastewater and sludge samples in Canada since late 1998. To date, BPA has been detected in all 24 h composite influent and effluent samples collected from sewage treatment plants with both primary (sedimentation) and secondary (activated sludge) treatment facilities. Although the levels of BPA in these wastewater samples ranged from 49.9 to 0.031 μg/L ($n = 47$ from 14 sewage treatment plants across Canada), they were generally < 1 μg/L in the influent and < 0.3 μg/L in the effluent. These results also indicated that the reduction (from influent to effluent) of BPA ranged from 37 to 94% among the treatment plants. BPA has also been detected in all grab samples of raw and digested sewage sludge ($n = 51$) collected from 18 plants, with an overall concentration range of 36.7–0.104 μg/g on a dry weight basis. A few examples of BPA levels are listed in Table 3. Total ion current chromatograms of derivatized sample extracts are shown in Figure 3, A (influent) and B (sludge). The same procedures are also being applied to the monitoring of BPA in industrial wastewater as well as in pulp and paper mill effluents and sludge. A detailed description of the occurrence and fate of BPA in the Canadian environment will be reported elsewhere.

Conclusions

We have developed new analytical methods for the determination of BPA in sewage effluent and sludge samples. Compared with solvent extraction procedures, SPE and SFE in the preconcentration steps have been shown to be time- and solvent-efficient techniques. SPE and SFE have also produced quantitative recoveries of BPA at residue levels. Determination of the PFP and acetyl derivatives of BPA by GC/MS is more sensitive and selective than determinations by existing methods that do not use chemical derivatization. The methods described in this paper have been successfully applied to about 100 samples, and the results have suggested that the estrogenic compound BPA is ubiquitous in Canadian municipal wastewater and sludge.

Acknowledgments

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